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Total Petroleum Hydrocarbon in Selected Fish of Shatt Al-Arab River, Iraq

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Abstract This study represents the concentrations of TPH in six commercial *Luciobarbus xanthopterus*, *Ctenophyngodon idella*, *Cyprinus carpio*, *Tilapia zillii*, *Palaniza abu* and *Leuciscus vorax* from Shatt Al-Arab River. The highest concentrations of TPH were found in *Leuciscus vorax* in during Summer 21.52 ± 3.41 $\mu\text{g/g}$ (dry wt.) and the lowest in *Tilapia zillii* 2.47 ± 0.33 $\mu\text{g/g}$ (dry wt.), while highest concentrations during winter found in *Cyprinus carpio* 8.2 ± 1.0 $\mu\text{g/g}$ (dry wt.), which is more than other fishes and the low concentration 0.33 μg were found in *Tilapia zillii* with level of $2.47 \pm \text{g}$ (dry wt.). The concentration in fish samples ordering as the following: *Luciscus vorax* > *Cyprinus carpio* > *Ctenophyngodon idella* > *Luciobarbus xanthopterus* > *Palaniza abu* > *Tilapia zillii*. This is may be due to the variety of fish feeding habitat and the season of reproduction, also the hydrocarbons found in the fish species of Shatt Al-Arab river are due to food and water sources, type of habitat, environmental factors, and lipid content.

Keywords Total petroleum hydrocarbons; Fishes; Shatt AL-Arab; Iraq

Introduction

The Iraqi freshwater environment, suffered from various types of pollution especially that related to pesticides, hydrocarbons or heavy metal toxicants. The numerous of oil exploration and exploitation activities in economies that produce and consume oil products to appear crude oil pollution as a natural consequence (Osuagwu et al., 2013).

Hydrocarbons are a common and natural occurrence in the environment and varying concentrations in storm water and effluent water are not unusual. Hydrocarbons in water can be found as free floating, emulsified, dissolved, or adsorbed to suspended solids. A hydrocarbon, by definition, is one of a group of chemical compounds composed only of hydrogen and carbon. Typically, hydrocarbons are broken down into three main classes; aliphatic, alicyclic, and aromatics. Further sub-classes can also be defined. Simply stated though, hydrocarbons are organic compounds made up of hydrogen and carbon (Reeves, 2000).

Petroleum hydrocarbons (PHCs) originally from oil and its derivatives existing either naturally from seepage of crude oil (Klenkin et al., 2010), or anthropoginically as a result of human being activities (Heras et al., 1992; Al-Hejuje et al., 2015). This anthropoginically pollution is due mainly to accidental discharge human error, sabotage, transportation and other natural causes. there is a significant spillage of oil into the environment from a number of sources including damaged oil tankers, storage vehicles, leakages of oil pipelines, oil tankers overflow (Agbogidi, 2005; Osuagwu et al., 2013).

The diffusion of pollutants (pesticides, petroleum oils and trace elements and other pollutants) in the aquatic environment specially rivers can cause deleterious effects on biota, effects which are not visible and may come to light after a long period of time (Sharma and Cyril, 2007).

There is a potential environmental risk of spills when using these materials, contaminated water may present opportunities for research on the effects of PHCs on existing aquatic organisms such as zooplankton. Other sources of pollution by PHC's arise from the different types of waste and sewage (Heras et al., 1992).

The aquatic organisms swallow petroleum hydrocarbons from the aquatic environment either from the water or from the suspended solids or with food or sediment (Heras et al., 1992; GESAMP, 1993; Cripps and Priddle, 1995).

GESAMP (1993) and Al-Saad et al. (2003) stated that the hydrocarbon pollutants have indirect effects on fishes as they cause the destruction or death of aquatic grasses, aquatic plants, coral reefs, zooplankton and phytoplankton which are used as a source of protection for the growth of larvae and small fishes or as a food for these animals.

Among these aquatic organisms fishes are known to be most sensitive to hydrocarbon compounds, leading to several specific and non-specific responses by their immune system. The specific responses may be intended to production of antibodies, and the unspecific responses may involve effects on increased activities such as lysozyme and/or phagocytosis (Reynaud and Deschaux, 2006).

In Basrah city are producing and exporting about two million barrels, which in turn leads to increased pollution of the marine environment and spread to river water environment, especially where the Shatt al-Arab is characterized by many of the loading and discharge petroleum products areas. Present study provides information on total petroleum hydrocarbons (TPHs) in six commercial fish species from Shatt Al-Arab River in Basrah city which used in later studies.

1 Materials and Methods

Shatt Al-Arab formed by the confluence of the Euphrates and the Tigris River at Al-Qurnah in Basrah city of southern Iraq. The southern end of the river constitutes the border between Iraq and Iran down to the mouth of the river as it discharges into the Arabian Gulf. A variety of industries, including refineries and petrochemical complexes, from this area release their effluents into the water such as Abadan oil refinery there are number of ports where in the ship and cargo handling activities contribute to Shatt Al-Arab River.

Freshwater fish samples were collected during summer (June, July and August) and winter (December, January and February) (2014-2015). Six economic species of freshwater fish locations were collected with the help of local fisherman of the region from Shatt Al-Arab River, named and the morphometric measurements were taken immediately (Table 1).

Table 1 Detailed information of the collected fish samples from Shatt Al-Arab

Fish species	Common name	Habitat	Feeding habit	Coad, 2010	No. of fish	Total Weight (g)	Total Length (cm)	Fat (%)
<i>Luciobarbus xanthopterus</i>	Cattan	native	Carnivores		10	916	40	7.5
<i>Ctenophryngodon idella</i>	Gareeba	foreign	Herbivorous		18	1117	57	2.72
<i>Cyprinus carpio</i>	Samti	foreign	Omnivorous		30	1019	35	2.6
<i>Tilapia zillii</i>	Bultti	foreign	Omnivorous		60	75	15	2.5
<i>Palaniza abu</i>	Khishni	native	detritus and phytoplankton feeding	46	43	21	21	3.5
<i>Leuciscus vorax</i>	Shillig	native	Carnivores		30	750	35	2.5

Fish samples were stored in pollution-free sealed polythene covers and transported to the laboratory at Marine science center, in ice box and stored at -20°C in the deep freezer until analysis. Fish samples were taken out from the deep freezer, thawed, and well cleaned in tap water to remove any external dirt. Edible muscle tissue without the skin and bone were used in the chemical analysis. Information regarding species, lipid content, length and weight is presented in Table 1.

Muscle samples were freeze dried, then sample was ground, and twenty five grams weighed was packed in a thimble (Whatman) and desiccated overnight prior to extraction.

The desiccated thimble was extracted using Soxhlet apparatus with Methanol: Benzene solvent for 24 hours as the methods described by (Grimalt and Oliver, 1993). The solvent was reduced and an aliquot was taken for lipid estimation. Another aliquot was subjected to removal of other contaminants by passing the sample through silica gel-alumina column. The instrumental analysis of TPHs was carried with UV fluorescence, using Basrah crude oil standard. Quantification was performed at 310 and 360 nm as excitation and emission wavelengths, respectively (Moopam, 2005).

2 Results and Discussion

Information regarding species, the length, weight, Fat % and concentration of total petroleum hydrocarbons in the selected commercial fish species *Luciobarbus xanthopterus*, *Ctenophyngodon idella*, *Cyprinus carpio*, *Tilapia zillii*, *Palaniza abu* and *Leuciscus vorax* presented in Table 1 and Table 2.

Table 2 Levels (means \pm SD) and average of TPH ($\mu\text{g/g}$ dry wt.) during two seasons

Fish Species	Summer	Winter	Average
<i>Luciobarbus xanthopterus</i>	5.18 \pm 0.29	6.21 \pm 0.09	5.695
<i>Ctenophyngodon idella</i>	6.41 \pm 1.49	6.98 \pm 1.34	6.695
<i>Cyprinus carpio</i>	7.21 \pm 0.29	8.20 \pm 1.00	7.705
<i>Tilapia zillii</i>	2.47 \pm 0.33	3.10 \pm 0.20	2.785
<i>Palaniza abu</i>	3.43 \pm 0.35	4.05 \pm 0.95	3.74
<i>Leuciscus vorax</i>	21.52 \pm 3.41	5.12 \pm 0.32	13.32

The result in Table 2 show variation in total petroleum hydrocarbons among six fish species which was the highest in *Leuciscus vorax* in summer 21.52 \pm 3.41 $\mu\text{g/g}$ (dry wt.) and the lowest in *Tilapia zillii* 2.47 \pm 0.33 $\mu\text{g/g}$ (dry wt.), while in winter *Cyprinus carpio* was 8.2 \pm 1.0 $\mu\text{g/g}$ (dry wt.) more than other fishes and the low concentration was found in *Tilapia zillii* too with level 2.47 \pm 0.33 $\mu\text{g/g}$ (dry wt.). The mean of summer and winter is shown in Table 2 and Figure 1.

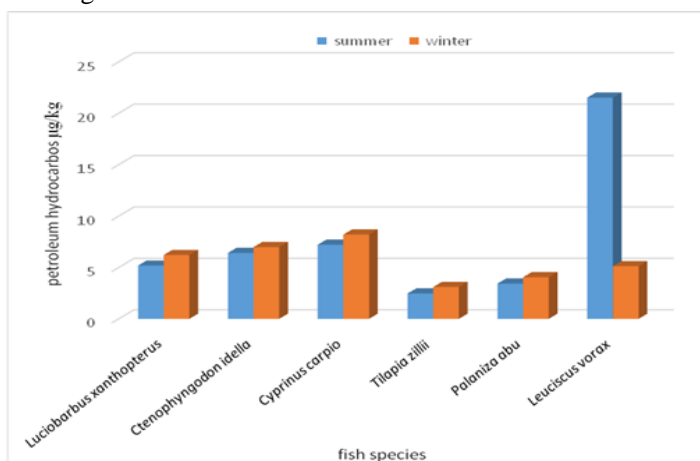


Figure 1 Petroleum hydrocarbon in fish species ($\mu\text{g/g}$ dry wt.) from Shatt Al-Arab River in summer and winter (2014-2015)

The percentage levels of TPH in fish were high in *Leuciscus vorax* 33% and *Tilapia zillii* have 7% lower than other fish. And according to the Figure 2 the fish ordering as the following: *Leuciscus vorax* > *Cyprinus carpio* > *Ctenophyngodon idella* > *Luciobarbus xanthopterus* > *Palaniza abu* > *Tilapia zillii*. This is may be due to the variety of fish feeding habitat and the season of reproduction. It is very common that fish and other aquatic have the ability to accumulation of petroleum products (Asuquo and Udoh, 2002).

The oil pollution of shatt Al-Arab due to the Industrial oil production activity and exploration and water Balance

discharge. Hydrocarbons as soluble or as tar particles can enter fish through the water, primarily through the gills or from their food by feeding on polluted prier (Al-Saad and Al-ASadi, 1989).

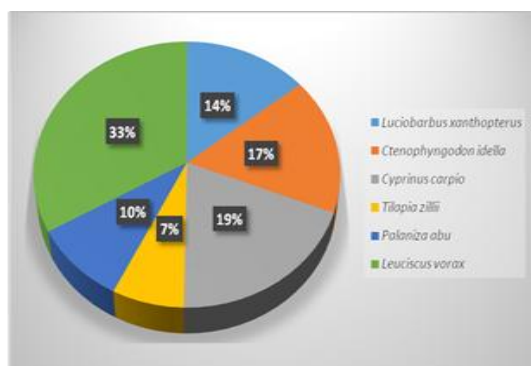


Figure 2 Average percentage of total petroleum hydrocarbons ($\mu\text{g/g}$ dry wt.)

In this study levels of TPH was close to or higher than as Salman (2011) reported in Um Al-Ward (2.46-3.23) $\mu\text{g/g}$; Al-Bagdadia (4.79-6.87) $\mu\text{g/g}$; Al-Nagarah (3.31-3.60) $\mu\text{g/g}$; Al-Bargah (1.51-2.76) $\mu\text{g/g}$. Due to increased oil activity in the Shatt al-Arab through the loading and unloading of ships and through the tides.

Atti (2014) reported the maximum value of petroleum hydrocarbons concentration in the muscles of green mullet *Liza subviridis* fish was recorded during winter (8.95 $\mu\text{g/g}$), whereas the highest value in the muscles of gold mullet *Liza klunzingeri* fish was recorded during spring (9.85 $\mu\text{g/g}$). The lowest values recorded in summer for both tissues in green and golden mullet fish in Shatt Al-Basrah. While (Al-Saad et al., 2015) found that the highest concentrations of *L. abu* species was 37.3 $\mu\text{g/g}$ dry weight during summer in the treatment unit station, while the lowest concentrations 4.81 $\mu\text{g/g}$ dry weight was recorded during spring in reference station. Whereas for *C. auratus* species the highest concentrations 29.303 $\mu\text{g/g}$ dry weight was recorded during autumn in the treatment unit station, while the lowest concentrations 2.51 $\mu\text{g/g}$ dry weight was recorded during spring in reference station they found that *L. abu* species have more ability to accumulate TPHs in their tissues compared with *C. auratus* species. Al-Ali et al. (2016) found that the levels of total Petroleum Hydrocarbons (TPH) in fourteen commercially important fish species from the Iraqi coastal water in North West Arabian Gulf during summer and winter (2014-2015). PHC residues in fourteen fish species varied between 2.45 and 6.85 $\mu\text{g/g}$ (dry wt.) in summer and 2.64 and 7.65 $\mu\text{g/g}$ (dry wt.) in winter. Among the fourteen *Tenuulosa ilisha* showed the highest level of TPH in both season summer and winter (6.85 \pm 0.29, 7.65 \pm 0.31 $\mu\text{g/g}$) respectively in the muscle tissue followed by *Euryglossa orientalis* (2.45 \pm 0.3, 2.64 \pm 0.06 $\mu\text{g/g}$) respectively also in both seasons. Also, we found that the *Leuciscus vorax* have the highest concentration of petroleum hydrocarbons compared with other fish.

Al-Saad et al. (2008) observed the mean concentrations of petroleum hydrocarbons in *Tenuulosa ilisha* fish were different due to its lengths and to the month in which has been capture. The lower mean concentration were observed during September in lengths (20 \pm 2 cm) value 0.29 $\mu\text{g/g}$ dry weight expressed as Basra crude oil equivalent, with fat content (45.51%), while higher values of petroleum hydrocarbons observed during March-May in lengths (40 \pm 2 cm) mean 8.89-5.34 $\mu\text{g/g}$ dry weight and high values of fat % (54.17-78.10) respectively.

Al-Saad et al. (2008) reported the hydrocarbons concentration decrease with the decrease of the lengths of fish and also during the months, this may be due to the fat contain of fish which differ in age stages. Asuquo and Udoh (2002) found the levels of total hydrocarbons in fish from Cross river Estuary in Nigeria greater than 6 (*Ethmalosa fimbriata* 6.91 \pm 0.37 and *Chrysichthys nigrodigitatus* 14.78 \pm 1.33 (ppm) and they found that depending on the season which was greater in wet season Al-Saad (1995) reported that many aquatic organisms of Shatt Al-Arab river including plants, algae, zooplankton, bacteria and fish were capable to synthesize biogenic hydrocarbons. There are many factors that affect the distribution of hydrocarbons in Shatt Al-Arab River (which accumulated later in the tissues of fish) such as, volatilization, mixing, flushing adsorption, chemical oxidation,

photo-decomposition, sedimentation, and biodegradation. These factors collectively reduce the concentration of hydrocarbons compounds (Al-Saad, 1995). Our data indicate that the level of Total petroleum Hydrocarbons which observed in selected fish lie within the range of values reported for comparable areas (Table 3).

Table 3 Comparison of petroleum hydrocarbon concentration ($\mu\text{g/g}$ dry wt.) in fish samples from Shatt Al-Arab River with those from selected marine areas

Stations	Conc. ($\mu\text{g/g}$)	References
Hor Al-Howaiza	1.09 - 11.11	Al-Khatib (2008)
Um Al-Ward	2.46 - 3.23	
Hor Al-Hammar, Iraq	1.945 - 4.011	Talal (2008)
Euphrates River, Nasiria City	6.01 - 13.63	Abed Ali (2013)
Southern Iraqi Marshes	1.15 - 27.42	Abdul Rehman (2010)
Al-Kahlaa River, Missan City	2.51 - 37.30	Al-Saad et al., (2015)
Al-Bagdadia	4.79 - 6.87	
Al-Nagarah	3.31 - 3.60	Salman (2011)
Al-Bargah	1.51 - 2.76	
Arabian Gulf	4.80 -7.40	Ashraf and Mian, (2010)
Shatt Al-Arab	29.60 -45.90	Al-Saad and Al-Asadi (1989)
Red Sea of Yemen	0.10 - 1.30	
Gulf of Aden	0.20 - 1.30	Nabil and Al-Shwafi (2008)
Arabian Gulf	0.57 - 3.67	Nozar et al.(2015)
Shatt Al-Arab estuary and NW Arabian Gulf	1.70 - 10.91	Al-Saad et al.(1997)
Shatt Al-Arab estuary and NW Arabian Gulf	2.60 - 12.55	Hantoush et al. (2001)
Khor Al-Zubair	8.30 - 40.60	Al-Saad (1990)
Iraqi Marine Water	11.44 - 48.16	Nasir (2007)
Al-Fao and Khor Abdullah	0.23 - 54.46	Al-Khion(2012)
Iraqi marine waters	2.55 - 7.25	Al-Ali et al.(2016)
Shatt Al-Arab	2.785- 13.32	Current study

3 Conclusions

The species of fish species from Shatt Al-Arab River were found to contain measurable amount of hydrocarbons. The hydrocarbons found in the species of fishes of Shatt Al-Arab River are due to food and water sources, type of habitat, environmental factors, and lipid content. we found that the *Leuciscus vorax* have the highest concentration of petroleum hydrocarbons compared with other fish. All this species are commercial and eaten by people, from the present study it can be concluded that TPH levels are not as high as could be expected in the Gulf, therefore, consumption of these fish species does not pose a significant health risk to the local population.

Authors' Contributions

Al-Ali B.S., Al-Anber L.J. and Al-Khion D.D. conceived and designed the experiments. Hantoush A.A., Saleh S.M., and Aleal A.H. analysed the data. AL-Saad,H.T and Al-Ali B.S. wrote the first draft of the manuscript. Al-Anber L.J. and Al-Khion D.D. contributed to the writing of the manuscript. Hantoush A.A., Saleh S.M., and Aleal A.H. agree with manuscript results and conclusions. AL-Saad,H.T and Al-Ali B.S. jointly developed the structure and arguments for the paper. AL-Saad H.T made critical revisions and approved final version. All authors reviewed and approved of the final manuscript.

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